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Reactions of Terminal Alkynes with a Bulky Dialkylaluminum Hydride: Hydroalumination versus Deprotonation

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In recent investigations we found an easy access to dialkyl(alkynyl)aluminum compounds by the deprotonation of phenylethyne with di(*tert*-butyl)- and dimethylaluminum hydride with evolution of molecular hydrogen. In contrast, the reactions of the bulky hydride $R_2Al{-}H$ [$R = CH(SiMe_3)_2$] with different alkynes $R{-}C{\equiv}C{-}H$ ($R = CMe_3$, $SiMe_3$, C_6H_5, H) yielded vinylic aluminum compounds, $R_2Al{-}CH{=}CH{-}R'$, by hydroalumination. Due to the effective steric shielding of the bulky alkyl substituents, the products were monomeric even in the solid state, with the alkenyl groups bonded to coordinatively unsaturated, tricoordinated aluminum atoms. Quantum-chemical calculations verified that there was no interaction between the π-electrons of the C=C bond and the vacant p-orbital at the coordinatively unsaturated aluminum atoms.

Introduction

Treatment of terminal alkynes with dialkyl hydrides of group 13 elements is a facile method for the preparation of alkynyl aluminum or gallium compounds with release of molecular hydrogen (eq 1).[1–3] Usually dimeric formula units were determined for these alkynyl derivatives in the solid state,[1,4] which adopted two different structural motifs[1] as borderline cases. One has the alkynyl groups perpendicular to the E−E axis of the central E_2C_2 heterocycle (E = Al, Ga), while the other involves a side-on coordination of the C≡C triple bond to the second metal atom. These aluminum[5] and gallium alkynyl derivatives are important starting compounds for the generation of interesting secondary products. For instance, dialkylaluminum alkynyls gave carbaalane clusters, e.g., $(AlMe)_8(CCH_2C_6H_5)_5H$, on treatment with the corresponding dialkylaluminum hydrides,[6] while alkynylgallium compounds afforded heteroadamantane-type molecules under similar conditions.[2]

$$2\,R_2E\text{-}H \;+\; 2\,H\text{-}C{\equiv}C\text{-}R' \xrightarrow{\qquad\qquad} (R_2E\text{-}C{\equiv}C\text{-}R')_2 \;+\; H_2 \qquad (1)$$

$R = Me, CMe_3; E = Al, Ga; R' = C_6H_5$
$R = Me, Et; E = Ga; R' = Me, nPr$

In previous experiments the deprotonation of terminal ethynes by dialkylaluminum hydrides was successful only with phenylethyne (eq 1). Early reports of such reactions showed that in some cases the addition of the Al−H bonds to the C≡C bond (hydroalumination) occurred instead.[7,8] The reaction courses appeared to be influenced by the solvent (donor vs nondonor solvent) and by the organic substituents of the terminal alkyne. However, in most cases the organoaluminum products were not isolated and characterized, but were destroyed by hydrolysis. Hence, secondary processes were not recognized. Recently novel carbaalane clusters[6] were found among such secondary products, as well as cyclophane-type molecules[9] and carbocations.[10] In order to systematically investigate the competition between hydrogen release and hydroalumination, we have conducted further reactions starting with the alkynes of the type H−C≡C−R.

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(1) Uhl, W.; Breher, F.; Haddadpour, S.; Koch, R.; Matar, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1839.

(2) Uhl, W.; Cuypers, L.; Neumüller, B.; Weller, F. *Organometallics* **2002**, *21*, 2365.

(3) Related synthetic procedures: (a) Cui, C.; Schmidt, J. A. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2002**, 2992. (b) Schiefer, M.; Reddy, D.; Ahn, H.-J.; Stasch, A.; Roesky, H. W.; Schlicker, A. C.; Schmidt, H.-G.; Noltemeyer, M.; Vidovic, D. *Inorg. Chem.* **2003**, *42*, 4970. (c) Zheng, W.; Mösch-Zanetti, N. C.; Roesky, H. W.; Hewitt, M.; Cimpoesu, F.; Schneider, T. R.; Stasch, A.; Prust, J. *Angew. Chem.* **2000**, *112*, 3229.

(4) (a) Tecle, B.; Ilsley, W. H.; Oliver, J. P. *Inorg. Chem.* **1981**, *20*, 2335. (b) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941. (c) Erker, G.; Albrecht, M.; Krüger, C.; Nolte, M.; Werner, S. *Organometallics* **1993**, *12*, 4979. (d) Almenningen, A.; Fernholt, L.; Haaland, A. *J. Organomet. Chem.* **1978**, *155*, 245. (e) Fries, W.; Schwarz, W.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1978**, *159*, 373.

(5) (a) Zheng, W.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **2002**, *2787.* (b) Uhl, W.; Er, E.; Matar, M. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1011. (c) Uhl, W.; Er, E.; Matar, M. *Main Group Chem.* **2006**, *5*, 31.

(6) (a) Uhl, W.; Breher, F. *Angew. Chem.* **1999**, *111*, 1578. (b) Uhl, W.; Breher, F.; Lützen, A.; Saak, W. *Angew. Chem.* **2000**, *112*, 414. (c) Uhl, W.; Breher, F.; Grunenberg, J.; Lützen, A.; Saak, W. *Organometallics* **2000**, *19*, 4536. (d) Uhl, W.; Breher, F.; Mbonimana, A.; Gauss, J.; Haase, D.; Lützen, A.; Saak, W. *Eur. J. Inorg. Chem.* **2001**, *3059*.

(7) (a) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375. (b) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1963**, *85*, 2165. (c) Eisch, J. J.; Kaska, W. C. *J. Organomet. Chem.* **1964**, *2*, 184. (d) Mole, T.; Surtees, J. R. *Aust. J. Chem.* **1964**, *17*, 1229. (e) Surtees, J. R. *Aust. J. Chem.* **1965**, *18*, 14. (f) Gavrilenko, V. V.; Palei, B. A.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *910.* (g) Miller, J. A. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman and Hall, 1993; p 373.

(8) (a) Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995. (b) Clark, G. M.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 527.

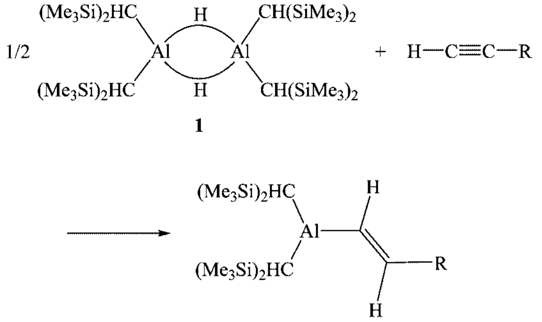
(9) (a) Uhl, W.; Hepp, A.; Matar, M.; Vinogradov, A. *Eur. J. Inorg. Chem.* **2007**, *4133.* (b) Uhl, W.; Breher, F.; Haddadpour, S. *Organometallics* **2005**, *24*, 2210. (c) Uhl, W.; Haddadpour, S.; Matar, M. *Organometallics* **2006**, *25*, 159. (d) Uhl, W.; Claesener, M.; Haddadpour, S.; Jasper, B.; Hepp, A. *Dalton Trans.* **2007**, *417*.

(10) (a) Uhl, W.; Vinogradov, A.; Grimme, S. *J. Am. Chem. Soc.* **2007**, *129*, 11259. (b) Uhl, W.; Grunenberg, J.; Hepp, A.; Matar, M.; Vinogradov, A. *Angew. Chem.* **2006**, *118*, 4465; *Angew. Chem., Int. Ed.* **2006**, *45*, 4358.

10.1021/om800190f CCC: $40.75

Results and Discussion

Reactions of H−Al[CH(SiMe$_3$)$_2$]$_2$ (1) with H−C≡C−R. The reactions of the alkynes R−C≡C−H (R = CMe$_3$, C$_6$H$_5$, SiMe$_3$) with the sterically encumbered dialkylaluminum hydride H−Al[CH(SiMe$_3$)$_2$]$_2$ (**1**) were complete after stirring at room temperature for 1 h. The NMR spectroscopic characterization of the colorless products (**2** to **4**, eq 2) clearly verified the formation of vinylic derivatives by addition of the Al−H bond to the C≡C bonds. In contrast to our earlier investigations involving phenylethyne[1] and the less shielded di(*tert*-butyl)- and dimethylaluminum hydrides, hydrogen release by deprotonation of the alkynes and formation of the corresponding alkynylaluminum product did not occur. Hydroalumination also occurred when gaseous ethyne, H−C≡C−H, was bubbled through a solution of **1** in *n*-hexane at low temperature (eq 2). After the usual workup, the product (**5**) was isolated as a colorless, highly viscous liquid, which could not be crystallized. However, its purity was sufficiently high to allow detailed NMR spectroscopic characterization. The hydroalumination reactions described here proceed much faster than the usually more selective hydrogallation reactions, which require reaction times of about 16 h in refluxing hexane for completion.[9,11,12]



(2)

2: R = CMe$_3$
3: R = C$_6$H$_5$
4: R = SiMe$_3$
5: R = H

The chemical shifts observed for the α-hydrogen atoms of bis(trimethylsilyl)methylaluminum groups (Al−C−H) in ^{1}H NMR spectra strongly depend on the coordination number of the aluminum atoms. While they are at about $\delta = 0$ to -0.5 for tricoordinated aluminum atoms, a shift to a higher field (below $\delta = -0.8$) occurs with tetracoordinated metal atoms.[13] Hence, the corresponding resonances of the products **2** to **5** [$\delta = -0.38$ (**2**), -0.31 (**3**), -0.35 (**4**), and -0.39 (**5**)] indicate monomeric formula units in solution. The vinylic proton signals of compounds **2** and **3** were observed as two doublets in the range $\delta = 6.0$ and 7.4 with coupling constants of 20.5 Hz, which is characteristic of a *trans*-arrangement of the hydrogen atoms at the 1,2-positions of a vinyl group. These results clearly indicate that the aluminum and hydrogen atoms of the starting hydride are in *cis*-positions at the C═C double bonds and that *cis/trans*-isomerization does not occur.[11,12] Both resonances due to the vinyl hydrogen atoms coincided in the case of the trimethylsilyl-substituted alkenyl compound **4** to give a broad singlet ($\delta = 7.27$). Only in that case were almost identical shifts also observed for the carbon atoms of the C═C double bond [^{13}C NMR: $\delta = 161.0$ (AlC) and 160.2 (SiC)]. As expected, the ^{1}H NMR spectrum of **5** showed three resonances of the chemically different vinylic hydrogen atoms, which had the characteristic coupling pattern [$^3J_{\mathrm{H-H}(cis)} = 16.4$ Hz, $^3J_{\mathrm{H-H}(trans)} = 21.4$ Hz, $^2J_{\mathrm{H-H}(geminal)} = 5.0$ Hz) of a −CH═CH$_2$ group. With the exception of some adducts we could not find references to isolated and thoroughly characterized vinylaluminum compounds of the type R$_{3-x}$Al(CH═CH$_2$)$_x$, although they were postulated and generated many times as intermediates in situ for transformations in organic chemistry.[14] It seems that hydroalumination was not involved in their syntheses.

According to the NMR spectroscopic characterization of the crude products, the compounds **2** and **3** were formed without any byproduct. However, the high solubility of **2** and **3** in noncoordinating solvents prevented their quantitative isolation by crystallization. The yields of the solid products were 75% and 44%, respectively. In contrast, the reaction of trimethylsilylethyne yielded a mixture of at least two products. Only one could be isolated and characterized by means of crystal structure determination (**4**, 25% yield). It has a structure similar to those of **2** and **3** with the hydrogen atoms in 1,2-position of the C═C double bond. The second product (**4a**) could not be isolated in pure form. However, the NMR spectroscopic data (see Experimental Section) gave clear evidence that it was an isomer of **4** in which the dialkylaluminum and the trimethylsilyl groups are attached to the same carbon atom, H$_2$C═C(AlR$_2$)(SiMe$_3$) [**4a**, R = CH(SiMe$_3$)$_2$]. In particular the small coupling constant between the vinyl hydrogen atoms (5.0 Hz) verified their geminal arrangement. These products were formed in a molar ratio of 1 to 0.1 (**4** to **4a**).

The course of this reaction gives insight into the relative directing effects of hydrogen atoms versus trimethylsilyl groups. In earlier investigations we observed a very high regioselectivity for such addition processes. Trimethylsilyl and dialkylaluminum groups had the strongest directing influence, and the aluminum atoms of the hydrides became attached exclusively to the carbon atoms in α-position to these groups. A further differentiation is not yet possible, because alkynes bearing ER$_2$ (E = Al, Ga) as well as SiMe$_3$ groups are not known. Phenyl groups have a weaker directing effect, and the weakest effect is observed for alkyl substituents. Mixtures of regioisomers as in the case of **4** and **4a** with the aluminum atoms on different carbon atoms of the C═C double bond have never been obtained before. From the results obtained in this study it may be concluded that hydrogen exerts a greater directive effect than SiMe$_3$. Thus, the following order of directing effect of substituents is operative: H > SiMe$_3$, ER$_2$ > aryl > alkyl.[15] Steric repulsion may be of minor importance only, because we did not observe the formation of a byproduct similar to **4a** [H$_2$C═C(AlR$_2$)(SiMe$_3$)] with the sterically less shielded phenylethyne.

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(11) Uhl, W.; Bock, H. R.; Breher, F.; Claesener, M.; Haddadpour, S.; Jasper, B.; Hepp, A. *Organometallics* **2007**, *26*, 2363.

(12) (a) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, *47*, 729. (b) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, *47*, 4463.

(13) (a) Uhl, W.; Matar, M. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1177. (b) Uhl, W.; Hannemann, F. *J. Organomet. Chem.* **1999**, *579*, 18. (c) Uhl, W.; Prött, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2259. (d) Uhl, W.; Hannemann, F. *Eur. J. Inorg. Chem.* **1999**, 201. (e) Uhl, W.; Spies, T.; Koch, R.; Saak, W. *Organometallics* **1999**, *18*, 4598.

(14) (a) Visser, H. D.; Oliver, J. P. *J. Organomet. Chem.* **1972**, *40*, 7. (b) Mandal, B. M.; Kennedy, J. P.; Kiesel, R. *J. Polym. Sci.* **1978**, *16*, 821. (c) Suzuki, H.; Yamazaki, N.; Kibayashi, C. *Tetrahedron Lett.* **2001**, *42*, 3013. (d) Rainier, J. D.; Cox, J. M. *Org. Lett.* **2000**, *2*, 2707. (e) Shojaei, H.; Li-Böhmer, Z.; von Zezschwitz, P. *J. Org. Chem.* **2007**, *72*, 5091. (f) Wiberg, K. B.; Cheeseman, J. R.; Ochterski, J. W.; Frisch, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6535. Related compounds: (g) Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; He, C.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M.; Merrill, W. A.; Power, P. P. *Angew. Chem.* **2005**, *117*, 5220. (h) Zhu, H.; Oswald, R. B.; Fan, H.; Roesky, H. W.; Ma, Q.; Yang, Z.; Schmidt, H.-G.; Noltemeyer, M.; Starke, K.; Hosmane, N. S. *J. Am. Chem. Soc.* **2006**, *128*, 5100.

(15) Eisch, J. J. In *Comprehensive Organic Synthesis Pergamon*; Frost, B., Flemming, I., Oxford, 1991; Vol. *8*, p 733.

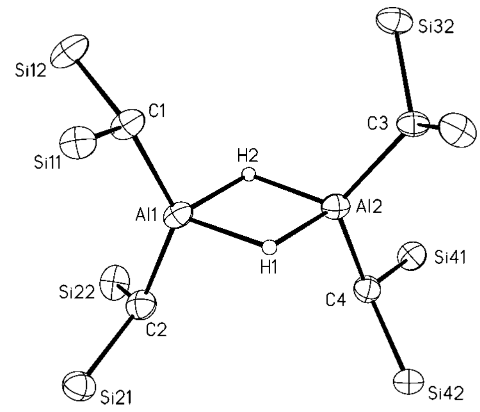

Figure 1. Molecular structure of **1**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(1) 1.963(4), Al(1)−C(2) 1.968(4), Al(1)−H(1) 1.78(3), Al(1)−H(2) 1.72(4), Al(1)−Al(2) 2.683(2), Al(2)−C(3) 1.975(9), Al(2)-C(3A) 1.96(2), Al(2)−C(4) 1.971(4), Al(2)−H(1) 1.72(4), Al(2)−H(2) 1.72(4), Al(1)−H(1)−Al(2) 100(1), Al(1)−H(2)−Al(2) 103(1), H(1)−Al(1)−H(2) 78(2), H(1)−Al(2)−H(2) 79(2).

Less bulky dialkylaluminum hydrides (R = CMe_3 and smaller) deprotonate the relatively acidic phenylethyne as described earlier.[1] Aliphatic alkynes gave complicated reaction mixtures from which crystals were obtained of the dimeric hydroalumination products, alkenyldialkylaluminum compounds, with the alkenyl groups in the bridging position. Similar compounds have been reported earlier.[8] Our NMR spectroscopic investigations showed, however, the occurrence of several isomers and dialkyl(alkynyl)aluminum derivatives. Hence, in these cases there is a competition between both reaction pathways. The complexity of these reactions is such that further study is required, but these preliminary results may be helpful for a short discussion.

We know from molecular weight determinations that **1** dissociates partially in solution to form a monomer/dimer equilibrium mixture. The monomers possess tricoordinate aluminum atoms; thus, the formation of an adduct with the π-system of the alkyne may occur as an initiating step in the hydroalumination reaction.[16] Addition of the Al−H bond to the C≡C bond may then follow.

Molecular Structures of Compounds 1 to 4. We published details of the synthesis and spectroscopic characterization of the dialkylaluminum hydride $H-Al[CH(SiMe_3)_2]_2$ (**1**) some years ago.[17] We have finally been able to obtain single crystals of **1** and to determine its crystal structure (Figure 1). It forms a dimer in the solid state via two Al−H−Al 3c-2e bonds. As expected for such dimeric formula units,[18,19] the transannular Al−Al distance in the planar Al_2H_2 heterocycle [2.683(2) Å] is relatively short and in the range of Al−Al single bonds.[20] The related, but sterically less encumbered compound di(*tert*-butyl)aluminum hydride is a trimer in the solid state and possesses an Al_3H_3 heterocycle.[21]

Crystal structure determinations of compounds **2** to **4** (Figures 2 to 4) verified the structures derived from NMR data. The

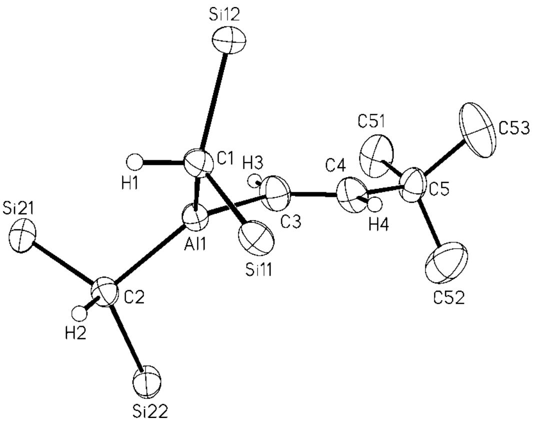

Figure 2. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups of the $CH(SiMe_3)_2$ substituents and the hydrogen atoms of the *tert*-butyl groups are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(1) 1.947(2), Al(1)−C(2) 1.953(2), Al(1)−C(3) 1.942(2), C(3)−C(4) 1.302(3), C(1)−Al(1)−C(2) 119.20(8), C(1)−Al(1)−C(3) 122.16(8), C(2)−Al(1)−C(3) 118.63(8), Al(1)−C(3)−C(4) 124.9(2).

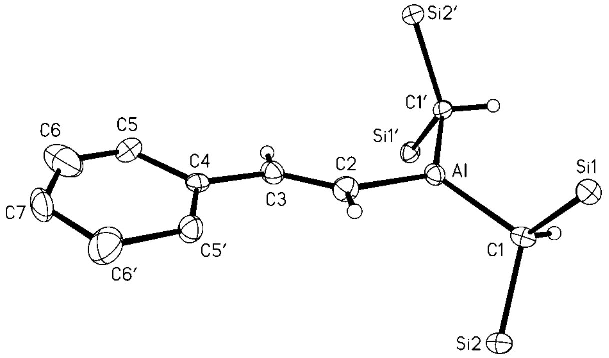

Figure 3. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(1) 1.945(3), Al(1)−C(2) 1.962(6), C(2)−C(3) 1.333(8), C(1)−Al(1)−C(1)′ 120.0(2), C(1)−Al(1)−C(2) 111.3(2), Al(1)−C(2)−C(3) 126.4(4); symmetry equivalent atoms generated by $-x$, $-y+2$, z.

aluminum atoms of the starting hydride R_2AlH **1** became attached exclusively to the β-carbon atom of the alkyne, and it was *cis*-addition that occurred. Owing to the effective steric shielding by two bulky bis(trimethylsilyl)methyl substituents, the products are monomeric even in the solid state. The sterically less shielded diisobutylalkenylaluminum compounds were reported to form dimers.[8] There is no indication from bond lengths that an interaction between the π-bond of the alkenyl group and the vacant p-orbital at the central aluminum atom plays a role in these compounds. The Al−C(alkenyl) bond lengths [1.942(2) to 1.962(6) Å] are similar to those of Al−C(alkyl) bonds [1.942(5) to 1.953(2) Å]. The C=C bond lengths [1.299(7) to 1.333(8) Å] are somewhat shorter than the standard value of 1.34 Å.[22] The AlC_2 planes including the α-carbon atoms of the bis(trimethylsilyl)methyl groups and the average planes of the aluminum alkenyl groups are not ideally coplanar. Angles between these planes are 48° (**2**), 21° (**3**), and 23° (**4**). Thus, the strongest deviation from the coplanar arrangement was observed for the *tert*-butyl compound **2**, which may be due to steric repulsion.

Quantum-Chemical Calculations. We conducted quantum-chemical calculations using density functional theory (DFT). In order to correctly describe the manifold of nonbonded

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(16) See mechanism of hydroboration: (a) ANagase, S.; Ray, N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536. (b) Seyferth, D. *Prog. Inorg. Chem.* **1962**, *3*, 129. (c) Streitwieser, A.; Verbit, L.; Bittman, R. *J. Org. Chem.* **1967**, *32*, 1530. (d) Üffing, C.; Ecker, A.; Koppe, R.; Merzweiler, K.; Schnöckel, H. *Chem.−Eur. J.* **1998**, *4*, 2142.

(17) (a) Uhl, W.; Cuypers, L.; Graupner, R.; Molter, J.; Vester, A.; Neumüller, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 607. (b) Uhl, W.; Matar, M. *Z. Naturforsch.* **2004**, *59b*, 1214.

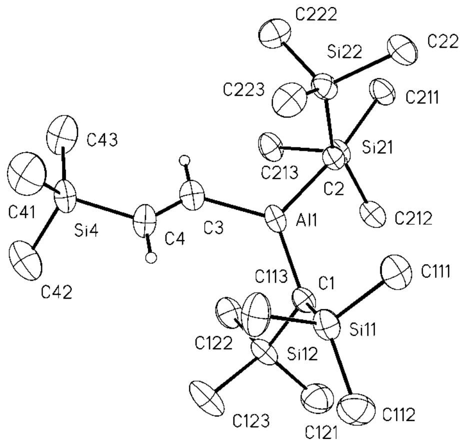

Figure 4. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl hydrogen atoms are omitted. Important bond lengths (Å) and angles (deg): Al(1)−C(1) 1.942(5), Al(1)−C(2) 1.952(4), Al(1)−C(3) 1.951(5), C(3)−C(4) 1.299(7), C(1)−Al(1)−C(2) 117.6(2), C(1)−Al(1)−C(3) 124.5(2), C(2)−Al(1)−C(3) 117.8(2), Al(1)−C(3)−C(4) 130.1(5).

Table 1. M05-2X/6-311G(d,p) Compliance Constants of 2, the Allylic Cation, and Ethene[a]

	C=C stretch	C=C torsion	R′−C stretch	R′−C torsion
$R_2Al-CH=CH-CMe_3$ **2**	0.110	1.923	0.423	80.1
$CH_2^+-CH=CH_2$	0.136	4.441	0.136	4.441
$H_2C=CH_2$	0.100	1.682		

[a] Torsional and stretching constants are in rad/mdyn and Å/mdyn, respectively [R′ = Al (compound **2**) or C].

interactions in **2**, we used the new hybrid meta exchange−correlation functional, M05-2X,[23] and a 6-311G(d,p) basis set.[24] The structure optimizations in the gas phase were based on the complete bis(trimethylsilyl)methyl compound **2**. The calculated Al−C (1.952 vs 1.942 Å obtained experimentally for **2**) and C=C bond lengths (1.338 vs 1.302 Å) were reproduced with sufficient accuracy. Further, our gas-phase optimization preserved the small tilt across the Al−C(vinyl) bond. That means we can exclude crystal-packing effects as the reason for this distortion. The assignment of the ^{13}C NMR resonances of the ethenyl group could be verified ($\delta = 129$ vs 130 for the carbon atom of **2** attached to the aluminum atom and $\delta = 180$ vs 165 for the carbon atom attached to the *tert*-butyl group). Considering **2** as a hetero allyl system, the C−C rotational barrier would be a good measure of the π-stabilization. This is a convenient definition, but due to the steric crowding in **2**, there are significant changes in the system that accompany this rotation, and they also have an energetic consequence. We therefore chose the rotational and stretching potential constants (compliance constants) as a local property; that means we distort infinitesimally.[25] Table 1 summarizes the torsional and the stretching compliance constants for both the C=C bond and the Al−C bond, respectively. Note that a lower compliance constant is in line with a stronger bond (lower flexibility).We also included the theoretical data for a prototype of a delocalized π-bond, the allyl cation, and the unperturbed ethene itself.

Our calculations did not give any hint of a significant π-delocalization between the aluminum atom and the C=C double bond. While a pronounced weakening of the C=C bond is expected in the case of delocalization of π-electron density (see the allyl cation below), the strength of the C=C double bond in **2** (0.110 Å/mdyn) indicates only a minimal weakening of the bond in comparison with the unperturbed ethene (0.100 Å/mdyn). On the other hand, due to our calculations for the allyl cation showing a π-electron delocalization, the weakening is pronounced (0.136 Å/mdyn). The same trend holds for the torsional constants. In the case of π-electron delocalization, the C=C torsion should require a lower energy, while the Al−C torsion should be hindered. While our calculations revealed a little smaller rotational barrier of the C=C rotation in compound **2** (1.923 rad/mdyn) compared to ethene (1.682 rad/mdyn), the high Al−C rotational compliance constant of 80.1 rad/mdyn indeed excludes any significant π-electron delocalization from the C=C bond to the aluminum atom. This is in line with earlier studies on smaller model systems,[26] which also showed that the participation of electropositive atoms diminishes the interaction with a π-bond dramatically.

Experimental Section

All procedures were carried out under purified argon. *n*-Hexane and *n*-pentane were dried over $LiAlH_4$. $[(Me_3Si)_2HC]_2AlH$[17] and tBu_2AlH[17a,21] were obtained according to literature procedures. Commercially available $Me_3Si-C{\equiv}C-H$, $Me_3C-C{\equiv}C-H$, and $H_5C_6-C{\equiv}C-H$ were distilled over molecular sieves (4 Å). The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Reaction of $[(Me_3Si)_2HC]_2Al-H$ with $Me_3C-C{\equiv}C-H$: Synthesis of 2. A solution of $H-Al[CH(SiMe_3)_2]_2$ (**1**) (0.220 g, 0.636 mmol) in 5 mL of *n*-hexane was cooled to 0 °C, and 94 μL of *tert*-butylethyne (0.062 g, 0.759 mmol) was added. The mixture was warmed to room temperature and stirred for 1 h. After concentration and cooling of the solution to −45 °C, colorless crystals of **2** formed. Yield: 0.204 g (75%). Mp (argon, sealed capillary): 126 °C. Anal. Calcd $[C_{20}H_{49}AlSi_4]$ (428.9): C, 56.0; H, 11.5; Al, 6.3. Found: C, 55.5; H, 11.4; Al, 6.3. ^1H NMR (C_6D_6, 400 MHz): δ 6.55 (1 H, d, $^1J_{H-H} = 20.5$ Hz, Al-CH=C*H*), 6.03 (1

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(18) (a) Downs, A. J.; Greene, T. M.; Collin, S. E.; Whitehurst, L. A.; Brain, P. T.; Morrison, C. A.; Pulham, C. R.; Smart, B. A.; Rankin, D. W. H.; Keys, A.; Barron, A. R. *Organometallics* **2000**, *19*, 527. (b) Almenningen, A.; Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 2315. (c) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400. (d) Klein, C.; Nöth, H.; Tacke, M.; Thomann, M. *Angew. Chem.* **1993**, *105*, 923. (e) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611. (f) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694. (g) Janik, J. F.; Wells, R. L.; Rheingold, A. L.; Guzei, J. A. *Polyhedron* **1998**, *17*, 4101. (h) Wehmschulte, R. J.; Ellison, J. F.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 6300.

(19) (a) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1986**, 805. (b) Baxter, P. L.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1990**, 2873. (c) Uhl, W.; Cuypers, L.; Geiseler, G.; Harms, K.; Massa, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1001. (d) Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113*, 5149.

(20) Uhl, W. *Adv. Organomet. Chem.* **2004**, *51*, 53.

(21) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *570*, 37.

(22) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

(23) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(24) Geometry optimizations, calculations of frequencies, and NMR parameters (B3LYP 6-31G(d) GIAO) were conducted with the Gaussian program package: Frisch, J.; et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2003. The generalized compliance constants were calculated with the program *Compliance* (K. Brandhorst, J. Grunenberg, Braunschweig, 2005) and are based on the B3LYP/6-13G(d) Cartesian force constants. For details of that method see: Frantzius, G. v.; Streubel, R.; Brandhorst, K.; Grunenberg, J. *Organometallics* **2006**, *25*, 118.

(25) Brandhorst, K.; Grunenberg, J. *ChemPhysChem* **2007**, *8*, 115.

(26) (a) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9287. (b) Wiberg, K. B.; Cheeseman, J. R.; Ochterski, J. W.; Frisch, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6535.

Table 2. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds 1 to 4

	1	2	3	4
formula	$C_{28}H_{78}Al_2Si_8$	$C_{20}H_{49}AlSi_4$	$C_{22}H_{45}AlSi_4$	$C_{19}H_{49}AlSi_5$
cryst syst	monoclinic	monoclinic	tetragonal	triclinic
space group	$P2_1/c$	$P2_1/n$	$I4_1cd$	$P\bar{1}$
Z	4	4	8	2
temp, K	153(2)	153(2)	100(2)	153(2)
D_{calcd}, g/cm^3	1.017	0.961	1.046	0.969
a, Å	12.3162(7)	10.0479(2)	15.4927(4)	10.5540(3)
b, Å	42.191(2)	12.8181(2)	15.4927(4)	12.1864(5)
c, Å	9.3853(5)	23.5244(4)	23.7644(6)	12.5117(5)
α, deg	90	90	90	97.449(2)
β, deg	111.791(3)	101.950(1)	90	95.133(2)
γ, deg	90	90	90	105.461(2)
V, 10^{-30} m^3	4528.4(4)	2964.16(9)	5704.0(3)	1524.9(1)
μ, mm^{-1}	2.718	2.150	2.259	2.467
cryst dimens, mm	0.11 × 0.04 × 0.02	0.28 × 0.14 × 0.10	0.36 × 0.26 × 0.18	0.17 × 0.05 × 0.04
radiation	Cu Kα; graphite-monochromator			
θ range, deg	2.09 − 72.67	3.84 − 72.66	5.49 − 70.24	3.59 − 72.28
index ranges	$-14 \le h \le 12$ $-45 \le k \le 51$ $-8 \le l \le 10$	$-12 \le h \le 11$ $-15 \le k \le 15$ $-28 \le l \le 27$	$-16 \le h \le 18$ $-16 \le k \le 18$ $-28 \le l \le 27$	$-12 \le h \le 12$ $-15 \le k \le 13$ $-12 \le l \le 14$
no. of unique reflns	8154 [R_{int} = 0.0712]	5648 [R_{int} = 0.0415]	2536 [R_{int} = 0.0823]	5070 [R_{int} = 0.0530]
no. of params	415	241	152	241
R1 (reflns $I > 2\sigma(I)$)	0.0577 (5108)	0.0445 (4659)	0.0419 (2204)	0.0846 (3435)
wR2 (all data)	0.1811	0.1309	0.0961	0.2918
max./min. residual electron density, 10^{30} e/m^3	0.647/−0.738	0.483/−0.355	0.412/−0.261	0.929/−0.640

H, d, $^1J_{H-H}$ = 20.5 Hz, AlCH=CH), 1.06 (9 H, s, CMe$_3$), 0.25 (36 H, s, $^1J_{H-Si}$ = 6.4 Hz, SiMe$_3$), −0.38 (2 H, s, $^1J_{H-Si}$ = 4.6 Hz, AlCHSi$_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 165.4 (AlCH=*C*H), 130.4 (br, Al*C*H=CH), 36.1 (*C*Me$_3$), 28.9 (C*Me*$_3$), 11.3 (AlCHSi$_2$), 4.2 ($^1J_{C-Si}$ = 50 Hz, Si*Me*$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −4. IR (CsBr plates, paraffin, cm^{-1}): 1568 vs, 1525 vw ν(C=C); 1464 vs (paraffin); 1404 s δ(CH); 1376 vs (paraffin); 1346 m, 1330 m, 1306 m δ(CH$_3$); 1112 vs, br ν(CC), δ(CH); 972 vw, 930 vw, 889 vw, 879 vw, 844 m, 815 m, 786 w, 763 w ρ(CH$_3$Si), δ(CC); 721 s (paraffin); 592 w, 561 m, 511 m, 481 s, 445 s ν(AlC). MS (EI, 20 eV) (%): 413 (2) [M$^+$ − Me], 345 (33) [Al{CH(SiMe$_3$)$_2$}$_2$]$^+$.

Reaction of [(Me$_3$Si)$_2$HC]$_2$Al−H with H$_5$C$_6$−C≡C−H: Synthesis of 3. A solution of H−Al[CH(SiMe$_3$)$_2$]$_2$ (**1**) (0.233 g, 0.673 mmol) in 30 mL of *n*-hexane was cooled to 0 °C, and 89 μL of phenylethyne (0.083 g, 0.81 mmol) was added. The solution was stirred at room temperature for 1 h. After concentration and cooling to −45 °C, colorless crystals of compound **3** formed. Yield: 0.133 g (44%). Mp (argon, sealed capillary): 104 °C. Anal. Calcd [$C_{22}H_{45}AlSi_4$] (448.9): C, 58.9; H, 10.1; Al, 6.0. Found: C, 59.4; H, 10.2; Al, 6.0. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.52 (2 H, pseudo-d, *ortho*-H of phenyl), 7.43 (1 H, d, $^2J_{H-H}$ = 20.6 Hz, AlCH=C*H*), 7.14 (2 H, m, *meta*-H of phenyl), 7.06 (1 H, m, *para*-H of phenyl), 6.99 (1 H, d, $^2J_{H-H}$ = 20.6 Hz, AlCH=CH), 0.27 (36 H, s, $^2J_{H-Si}$ = 6.3 Hz, SiMe$_3$); −0.31 (2 H, s, $^2J_{H-Si}$ = 4.6 Hz, AlCHSi$_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 151.5 (AlCH=*C*H), 139.4 (*ipso*-C of phenyl), 136.8 (Al*C*H=CH), 129.0 (*meta*-C of phenyl), 128.7 (*para*-C of phenyl), 126.8 (*ortho*-C of phenyl), 11.2 (AlCSi$_2$), 4,3 ($^1J_{C-Si}$ = 50 Hz, SiMe$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −4. IR (CsBr plates, paraffin, cm^{-1}): 1589 m, 1560 m phenyl, ν(C=C); 1454 vs, 1377 vs (paraffin); 1302 w, 1259 m, 1248 s δ(CH$_3$); 1207 vw, 1192 vw, 1173 w, 1155 w, 1069 w ν(CC); 1018 m δ(CH); 928 m, 845 vs, 775 m, 762 w ρ(CH$_3$Si), δ(CC); 721 s (paraffin); 683 w, 673 m ν_{as}(SiC); 611 vw ν_s(SiC); 559 w, 521 w, 476 w, 420 w ν(AlC).

Reaction of [(Me$_3$Si)$_2$HC]$_2$Al−H with Me$_3$Si−C≡C−H: Synthesis of 4. To a cooled (0 °C) solution of H−Al[CH(SiMe$_3$)$_2$]$_2$ (**1**) (0.244 g, 0.705 mmol) in 5 mL of *n*-hexane was added 119 μL of trimethylsilylethyne (0.083 g, 0.84 mmol). The mixture was stirred at room temperature for 1 h. A small quantity of a colorless, insoluble solid of unknown constitution precipitated and was filtered off. The solvent of the filtrate was removed under vacuum, and the oily residue was dissolved in a small quantity of *n*-pentane. Cooling to −28 °C afforded colorless crystalline **4**. Yield: 0.078 g (25%). Mp (argon, sealed capillary): 68 °C. Anal. Calcd [$C_{19}H_{49}AlSi_5$] (445.0): C, 51.3; H, 11.1; Al, 6.1. Anal. Found: C, 52.2; H, 11.0; Al, 6.3. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.27 (2 H, s, the resonances of both vinyl protons coincide), 0.24 [36 H, s, CH(Si*Me*$_3$)$_2$], 0.16 (9 H, s, C=C−Si*Me*$_3$, $^2J_{H-Si}$ = 6 Hz), −0.35 (2 H, s, $^2J_{H-Si}$ = 9,2 Hz, AlCHSi$_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 161.0 (Al*C*H=CH), 160.2 (AlCH=*C*H), 11.1 ($^1J_{C-Si}$ = 52 Hz, AlCSi$_2$), 4.2 [$^1J_{C-Si}$ = 50 Hz, CH(Si*Me*$_3$)$_2$], −1.8 (C=C−Si*Me*$_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −8 (C=C-SiMe$_3$), −4 [CH(SiMe$_3$)$_2$]. IR (CsBr plates, paraffin, cm^{-1}): 1578 vs, 1558 vs ν(C=C); 1456 vs (paraffin); 1404 m δ(CH$_3$); 1377 s (paraffin); 1304 w, 1248 s δ(CH$_3$); 1113 s, br. ν(CC); 1014 sh δ(CH); 930 w, 843 vs, 783 w ρ(CH$_3$Si); 719 s (paraffin); 671 w ν_{as}(SiC); 625 vw ν_s(SiC); 592 w, 559 w, 478 m, 393 m ν(AlC).

NMR Data of H$_2$C=C(SiMe$_3$)−Al[CH(SiMe$_3$)$_2$]$_2$, 4a. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.82 and 6.75 (each 1 H, d, $^2J_{H-H}$ = 5.0 Hz, H$_2$C=C). ^{13}C NMR (C_6D_6, 100 MHz): δ 146.4 (C=*C*H$_2$), 128.7 (*C*=CH$_2$); all remaining resonances could not be assigned unambiguously.

Reaction of [(Me$_3$Si)$_2$HC]$_2$Al−H with H−C≡C−H: Synthesis of 5. A solution of H−Al[CH(SiMe$_3$)$_2$]$_2$ (**1**) (0.245 g, 0.708 mmol) in 75 mL of *n*-hexane was cooled to −78 °C. Gaseous ethyne (dried over CaCl$_2$) was bubbled through the solution for 10 min. The mixture was slowly warmed to room temperature. All volatiles were removed under vacuum. Product **5** remained as a colorless, highly viscous, resin-like substance, which could not be crystallized from different noncoordinating solvents. The ^{1}H NMR spectrum of the crude product showed essentially the resonances of **5**. Some signals of low intensity indicate the formation of only small quantities of unknown impurities. Elemental analysis was not conducted owing to the missing purification and the difficult handling of the highly viscous product. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.56 [1 H, dd, $^3J_{H-H(cis)}$ = 16.4 Hz, $^3J_{H-H(trans)}$ = 21.4 Hz, Al-C(H)=C], 6.37 [1 H, dd, $^3J_{H-H(trans)}$ = 21.4 Hz, $^2J_{H-H(geminal)}$ = 5.0 Hz, *cis*-Al-C=C−H], 6.06 [1 H, dd, $^3J_{H-H(cis)}$ = 16.4 Hz, $^2J_{H-H(geminal)}$ = 5.0 Hz, *trans*-Al-C=C-H], 0.21 [36 H, s, CH(Si *Me*$_3$)$_2$], −0.39 (2 H, AlCHSi$_2$). ^{13}C NMR (C_6D_6, 100 MHz): δ 148.4 (Al *C*H=CH), 138.6 (AlCH=*C*H), 11.1 (AlCSi$_2$), 4,2 [CH(Si*Me*$_3$)$_2$]. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −3.7. IR (CsBr plates, neat, cm^{-1}): 2953 m, 2897 w, 2852 m (CH); 1506 s ν(C=C); 1463 m, 1435 m, 1402 vw, 1249 s δ(CH_3); 1205 vw, 1195 vw, 1101 w; 1014 m δ($CHSi_2$); 929 w, 844 m, 779 vw, 750 w, 729 vw ρ(CH_3Si); 671 m ν_{as}(SiC); 646 m, 611 w ν_s(SiC); 559 w, 524 w, 476 w, 451 w, 397 w, 374 w ν(AlC).

Crystal Structure Determinations of Compounds 1 to 4. Single crystals were obtained by repeated recrystallization from *n*-hexane (20/−15 °C; **1**) or from the reaction mixtures (**2** and **3**: *n*-hexane at −45 °C; **4**: *n*-pentane at −28 °C). The crystallographic data were collected with Bruker APEX and Bruker Smart 6000 diffractometers. The structures were solved by direct methods and refined with the program SHELXL-97[27] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters, and structure refinement details are given in Table 2. One bis(trimethylsilyl)methyl group of **1** (C3) showed a disorder. The carbon atom C3 and the methyl groups attached to Si31 were refined on split positions with occupation factors of 0.67 to 0.33 and restrictions of bond lengths and angles. The molecule of compound **3** is located on a crystallographic 2-fold rotation axis with Al1 and C7 on special positions. Due to the special position of the molecule, the phenylethenyl group showed a disorder across the 2-fold rotation axis, and the atoms C2, C3, C4, and C5/C5A were refined with occupancy factors of 0.5. The quality of the crystals of compound **4** was relatively poor; nevertheless the data were included in this article because they give clear structural evidence. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-652260 (**1**), -652261 (**2**), -652263 (**3**), and -652262 (**4**).

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Supporting Information Available: CIF files giving the crystal data for compounds **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] *SHELXTL-Plus*, Rel. 4.1; Siemens Analytical X-Ray Instruments Inc.: Madison, WI, 1990. Sheldrick, G. M *SHELXL-97, Program for the Refinement of Structures*; Universität Göttingen: Germany, 1997.